INVESTIGATION OF SOIL CONTAMINATION AS A RESULT OF AN ALLEGED DISCHARGE OF LEAD-ACID BATTERY SOLUTION AT ERIE BATTERY INC., PORT COLBOURNE, 1991

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INTRODUCTION

On April 30, 1991, the Phytotoxicology Section received a request from the Welland District Office of the Ministry of the Environment to investigate possible soil contamination resulting from an alleged discharge of a contaminant to the ground. The suspected contaminant was sulphuric acid recovered from lead-acid storage batteries by Erie Battery Inc. This company is engaged in processing waste batteries by draining the acid, breaking the cases and recovering the lead plates and casing plastic. The acid is retained in a storage tank for removal by a waste hauler. The lead and plastic case material is removed from the property for refining and recycling.

On May 8, 1991, William Gizyn of the Phytotoxicology Section, accompanied by John Neamtz of the Welland District Office, visited the Erie Battery property located at 28 Invertose Drive in Port Colborne, Ontario. Taylor Gordon, who introduced himself as an employee of the company, acknowledged that in January, 1991, liquid that had accumulated in the well of a truck loading dock was pumped out and discharged to an area adjacent to the west side of the Erie Battery building. According to Mr. Gordon, 100 feet of two inch diameter fire hose was used for this task.

The intent of this investigation was to ascertain if this discharged liquid contained lead-acid battery solution.

SITE DESCRIPTION

Invertose Drive is an east-west road located in a recently developed industrial area of Port Colborne. Aerial photography of this area flown in 1978, shows a mixture of wooded areas and abandoned agricultural fields. Aerial photography obtained in 1983 shows the road, the Erie Battery facility, as well as other industrial facilities to the east. Since the Erie Battery facility was constructed on the site of an agricultural field, it is highly improbable that soil would have been historically

contaminated by materials associated with a lead-acid battery processing operation (eg., lead, antimony, sulphate, reduced soil pH).

The Erie Battery building is oriented along a north-south axis. A concrete loading platform abuts the building at the south end. Integral to this platform is a loading dock for use by trucks. Since the platform is at ground level, the loading dock slopes downward to the platform, forming a concrete-walled and gravel-bottom well that would be prone to filling with rainwater.

Approximately 20 metres west of the building is the apparent boundary line of a long-abandoned agricultural field, now covered with woody shrubs and small trees. Buckthorn shrubs dominated the edge of this vegetation.

The whole area is relatively flat, with micro-drainage patterns that were mechanically created. Immediately east of this shrub area is a very shallow ditch (no more than 20 centimetres deep). Drainage from the west part of the Erie Battery property would be to the north, along this shallow ditch. Between the south end of the building and the ditch, there was evidence of soil disturbance. An earth pile approximately one metre high, and low, bulldozed areas devoid of any vegetation, were present. These landscape characteristics are illustrated in Figure 1.

SOIL SAMPLING SITES AND PROCEDURES

The selection of sample sites was based on the scenario provided by Mr. Gordon, along with an assessment of the probable path of any contaminant discharge. Sites unlikely to have been influenced by such a discharge were also selected. A total of 10 sites were sampled. A sample site consisted of an area 0.25 m^2 in size. A single sample consisted of 10 to 12 soil cores 1.5 centimetres in diameter to a depth of five centimetres.

The locations of the sample sites are indicated in Figure 1. Table 1 lists the sites, describes the site and its location, and presents the rationale for sampling at that point.

FIGURE 1: SKETCH MAP SHOWING THE LOCATION OF SOIL SAMPLING SITES AT ERIE BATTERY INC., MAY 8, 1991

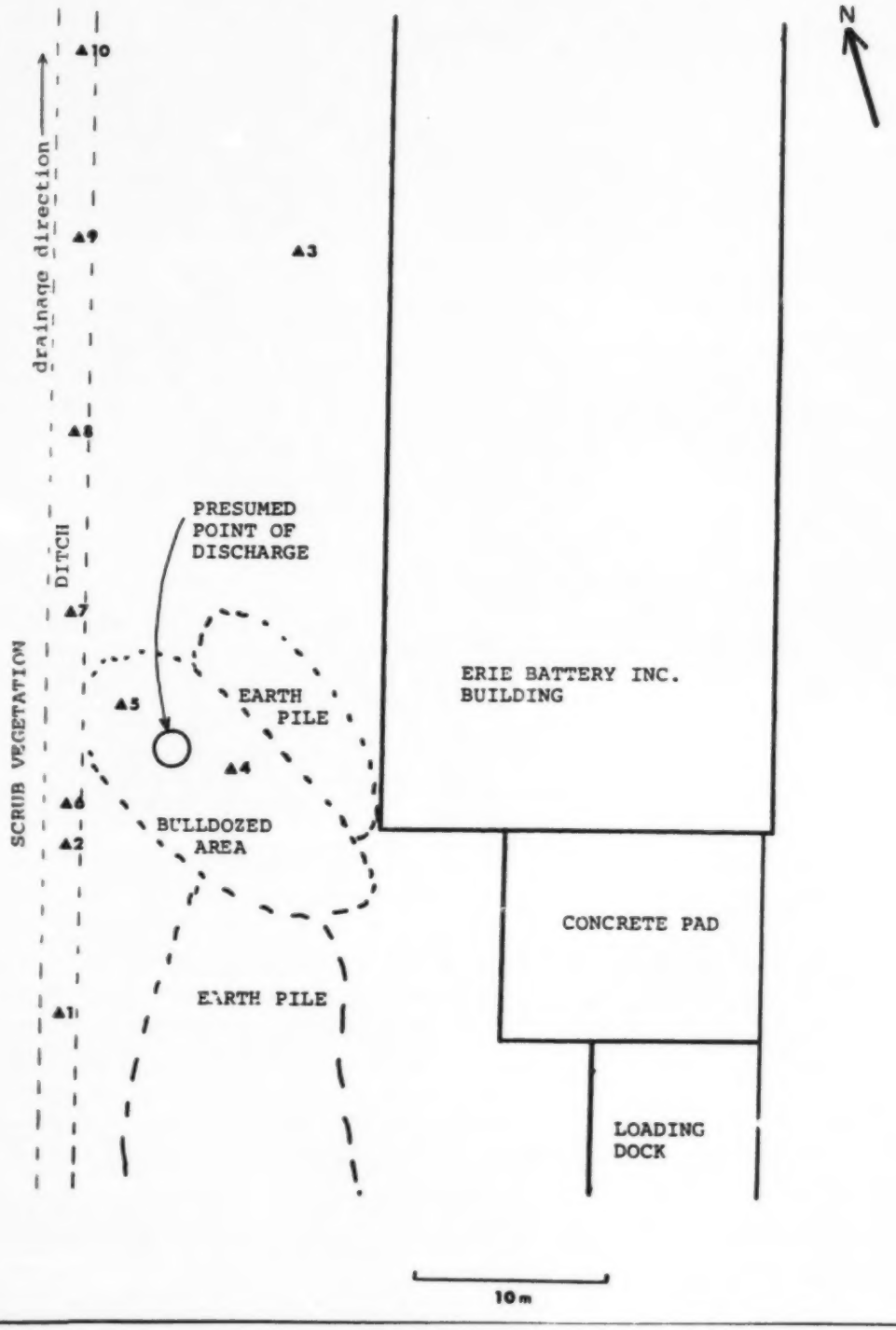


TABLE 1: DESCRIPTION AND SELECTION RATIONALE OF SOIL SAMPLE SITES

Site No.	Site Description	Site Selection Rationale
1	Ditch site south of and uphill from the point where discharge would have entered the ditch	A site in the ditch that would not have been affected by alleged contaminant discharge
2	Ditch site near the point where discharge would have entered the ditch	A site in the ditch that may have been affected by alleged contaminant discharge
3	Site five metres from west wall and mid-way point along length of building	A site that would not have been affected by alleged contaminant discharge
4	Bulldozed area site between building and presumed point of discharge	A site in the bulldozed area that was unlikely to have been affected by alleged contaminant discharge
5	Bulldozed area site between presumed point of discharge and the ditch	A site in the bulldozed area that was probably affected by alleged contaminant discharge
6	Ditch site near the point where discharge would have entered the ditch	A site in the ditch that was probably affected by alleged contaminant discharge
7	Ditch site downhill and 10 metres from Site 6	A site in the ditch along the flowpath of alleged contaminant discharge
8	Ditch site downhill and 10 metres from Site 7	A site in the ditch along the flowpath of alleged contaminant discharge
9	Ditch site downhill and 10 metres from Site 8	A site in the ditch along the flowpath of alleged contaminant discharge
10	Ditch site downhill and 10 metres from Site 9	A site in the ditch along the flowpath of alleged contaminant discharge

As each sample was collected, a field sample number-label was attached and the sampling location was marked on a field sketch. To prevent cross contamination by sampling equipment, the sampling corer was inserted into the soil at each subsequent site several times and these cores discarded. The sample was then collected. All samples remained within sight of the investigator, or in a locked vehicle, until delivered to the Phytotoxicology Section processing laboratory.

SAMPLE PROCESSING AND ANALYSIS

Samples were allowed to air dry in a locked room. They were subsequently sieved through a 2 mm mesh screen. The fraction that passed through the screen was ground by agate mortar and pestle until it passed through a 355 um screen. Prepared samples were delivered to the Laboratory Services Branch (LSB), under seal, following continuity of possession procedures.

Samples were analyzed for those parameters indicative of a discharge of lead-acid battery solution. Details of analytical procedures are available from the QA/QC office of LSB. General descriptions of the methods follow.

LEAD The 355 um fraction of soil was extracted with full strength aqua regia (HCl and H_2NO_3). The extract was analyzed by flame atomic absorbtion spectrophotometry.

ANTIMONY The 355 um fraction of soil was extracted with full strength aqua regia (HCl and H_2NO_3). The extract was analyzed by hydride generator atomic absorbtion spectrophotometry.

SULPHUR The 355 um fraction of soil was analyzed by a LECO™ induction furnace sulphur analyzer.

SULPHATE The 355 um fraction of soil was extracted with distilled water and the extract analyzed for sulphate ions by an ion chromatograph.

pH pH of the 2 mm fraction of soil in a $CaCl_2$ solution was determined by a hydrogen ion electrode.

Each sample was analyzed twice. Means of the analyses were reported in "Certificates of Analysis", copies of which comprise Appendices 1 and 2.

ANALYTICAL RESULTS

The contents of the Certificates of Analysis are reproduced in the Table 2. Field sample numbers and site numbers, as previously described, have been added to the respective laboratory sample numbers.

TABLE 2: RESULTS OF CHEMICAL ANALYSES OF SOIL COLLECTED AT ERIE BATTERY INC., PORT COLBORNE

Laboratory Sample Number	Field Sample Number	Site Number	Lead (mg/Kg)	Antimony (mg/Kg)	Sulphur (%)	Sulphate (mg/Kg)	pH
CC20-0022	5046	1	44	0.4	0.032	210	6.18
CC20-0023	5047	2	**260**	**9.2**	0.099	2300	3.17
CC20-0024	5048	3	45	0.4	0.052	1400	7.16
CC20-0025	5049	4	82	0.8	0.092	2000	6.49
CC20-0026	5050	5	**440**	**3.4**	**0.15**	4200	5.24
CC20-0027	5051	6	**840**	**13**	**0.24**	6800	2.72
CC20-0028	5052	7	**760**	**4.2**	0.10	2900	4.33
CC20-0029	5053	8	100	0.9	0.036	880	4.98
CC20-0030	5054	9	**360**	**2.0**	0.047	1100	5.20
CC20-0031	5055	10	**380**	**3.7**	**0.15**	4500	4.20
ULN[1] rural			150	1	0.1	NE[2]	NE[2]
ULN[1] urban			500	8	NE[2]	NE[2]	NE[2]

[1] Phytotoxicology Upper Limit of Normal (ULN) Guideline
[2] ULN not established

BOLD = rural ULN exceeded **BOLD** + **UNDERLINE** = urban ULN exceeded

Highlighted in Table 2 are individual results which exceed the Phytotoxicology Upper Limit of Normal Guidelines for rural and urban soil, where such guidelines have been established. An explanation of the ULN guidelines can be found in Appendix 3.

DISCUSSION

The concentrations of lead, antimony, sulphur and sulphate vary widely, as much as an order of magnitude. The range in soil solution pH is extreme, indicating areas of severe acidification. Since pH is expressed on a logarithmic scale, the range is over four orders of magnitude. Such extreme variability is, by itself, indicative of deposition of a contaminating material to the soil in an irregular pattern.

Concentrations of lead, antimony, sulphur and sulphate are concurrently elevated at many sites. Site 6, which is at or near the point where the discharge would have entered the ditch, had the highest lead, antimony, sulphur and sulphate concentrations, and the lowest soil pH.

Since the Erie Battery property was, until recently, an agricultural area, soil concentrations of the contaminants could be compared to rural ULN guidelines. By doing so, it is clear that most of the sites where the discharge would have flowed have concentrations which exceed the rural ULN. Some of these sites have lead and antimony concentrations that even exceed the urban ULN.

In order to demonstrate the relationships between the five analytes, a series of scatter plots were generated that would relate each pair of analytes. Ten such permutations are possible. Figures 2a through 2j represent the relationships between each pair.

To assess the significance of the apparent correlations that exist between the analyte pairs, correlation tests were performed and the R^2 values and the statistical levels of significance are reported in Table 3.

TABLE 3: R^2 AND SIGNIFICANCE FOR ANALYTE PAIRS		
Analyte Pair	R^2	Significant at
Lead-Antimony	0.510	p=0.05
Lead-Sulphur	0.570	p=0.05
Lead-Sulphate	0.613	p=0.01
Lead-pH	0.524	p=0.05
Antimony-Sulphur	0.630	p=0.01
Antimony-Sulphate	0.581	p=0.05
Antimony-pH	0.786	p=0.01
Sulphur-Sulphate	0.982	p=0.01
Sulphur-pH	0.437	p=0.05
Sulphate-pH	0.433	p=0.05

Figure 2a:

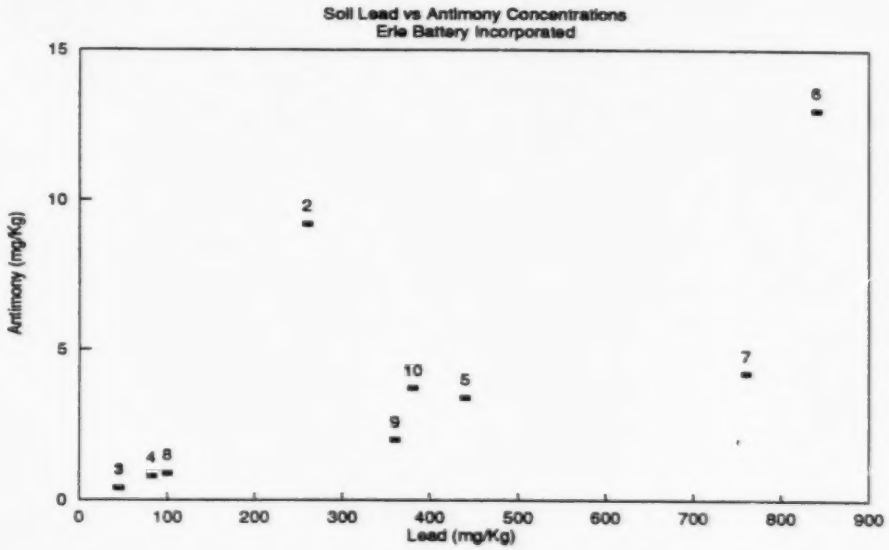


Figure 2b:

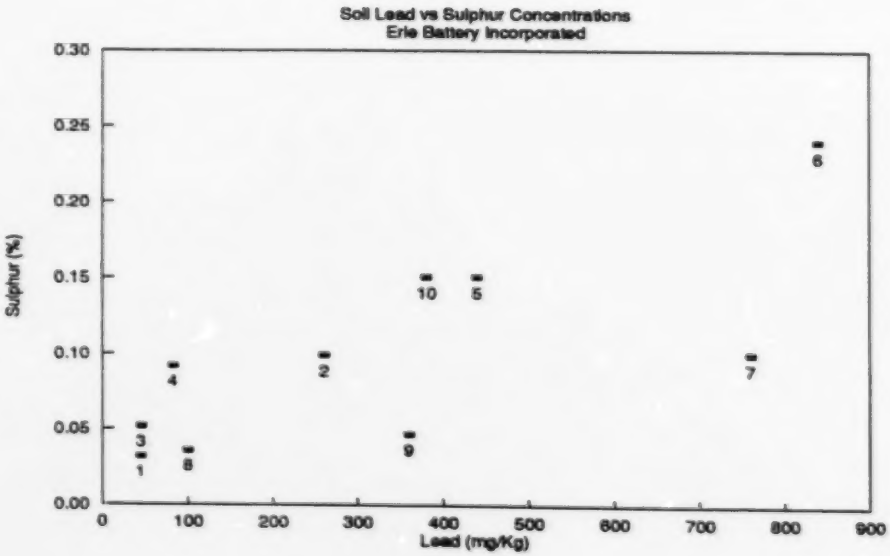


Figure 2c:

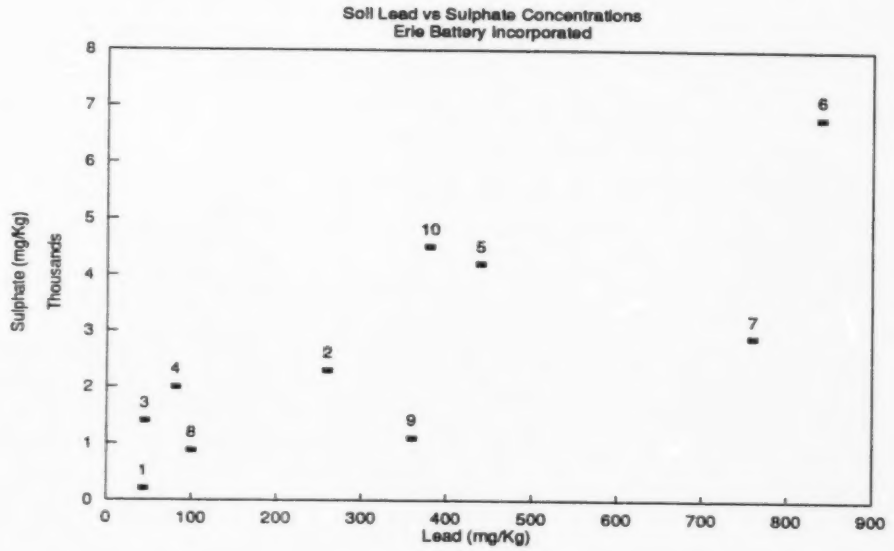


Figure 2d:

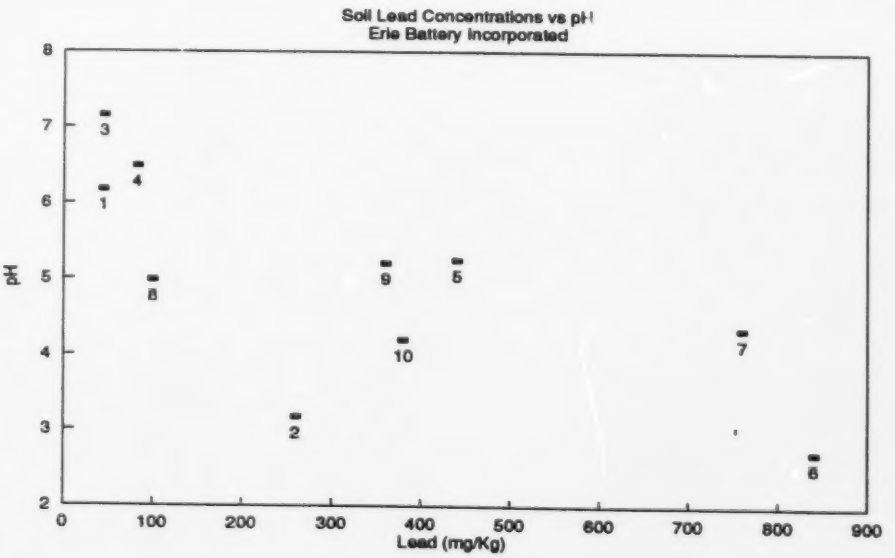
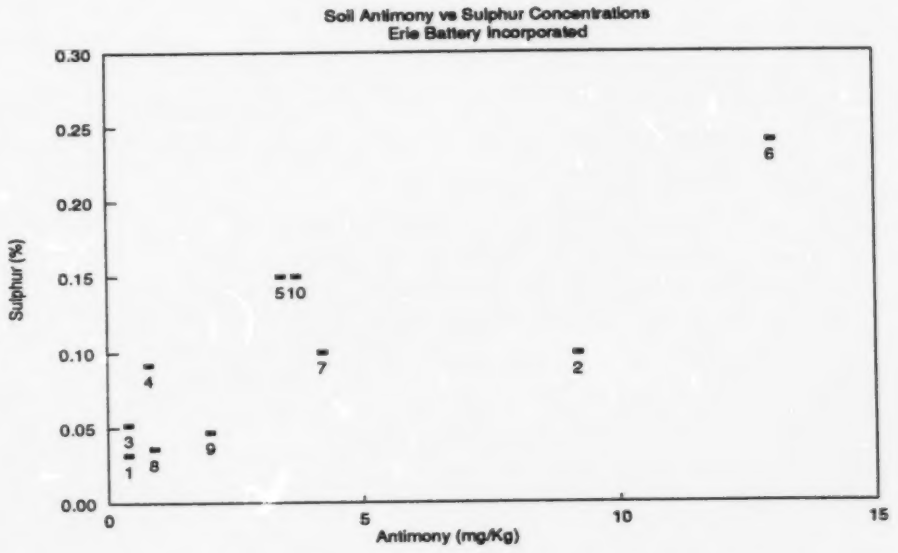


Figure 2e:



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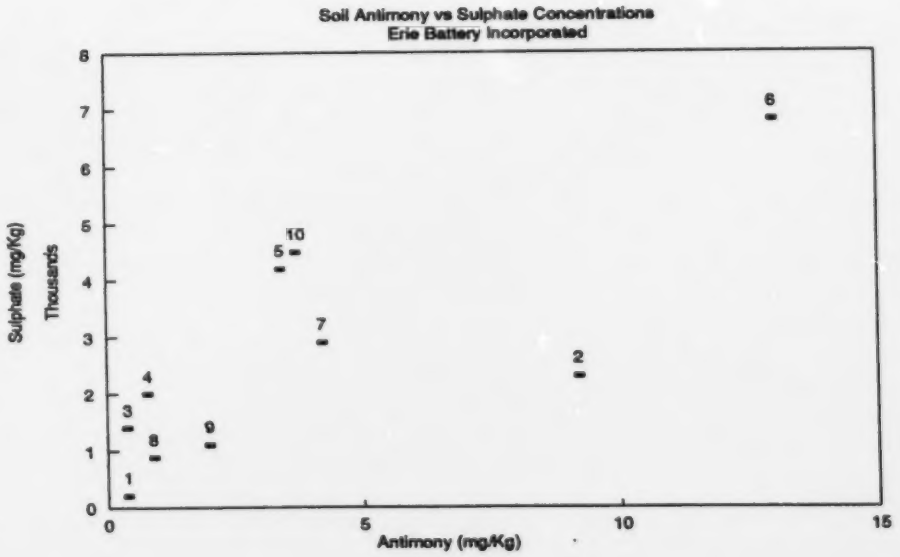

Figure 2g:

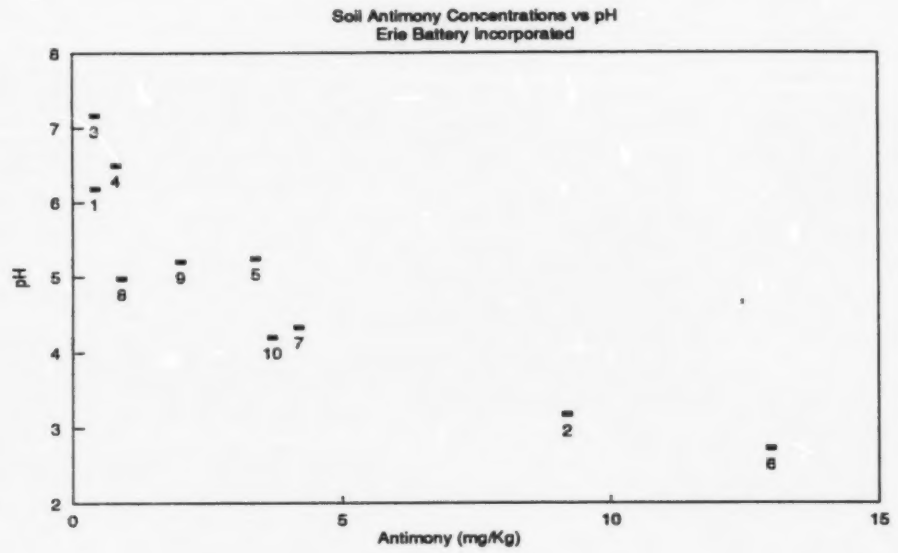

Figure 2h:

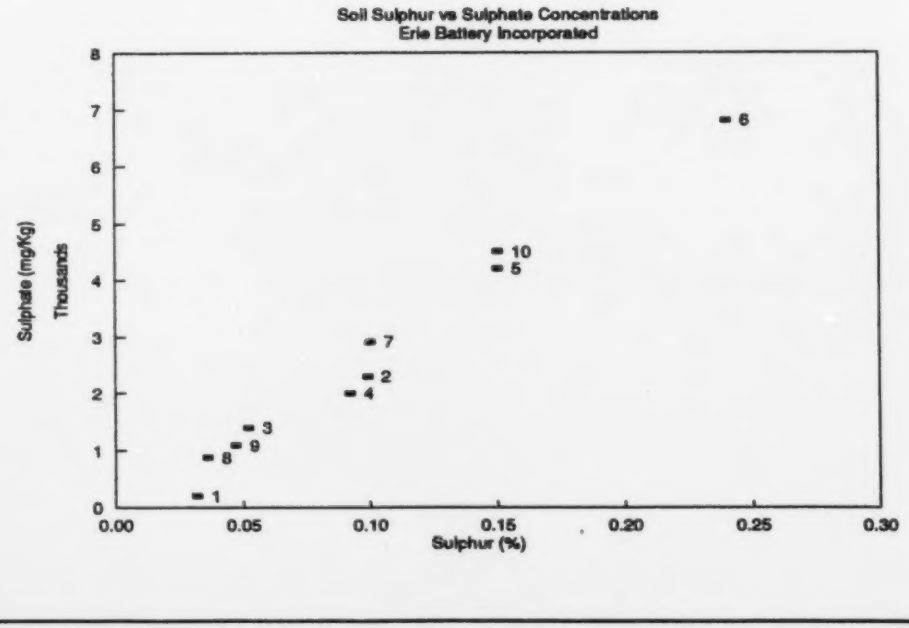

Figure 2i:

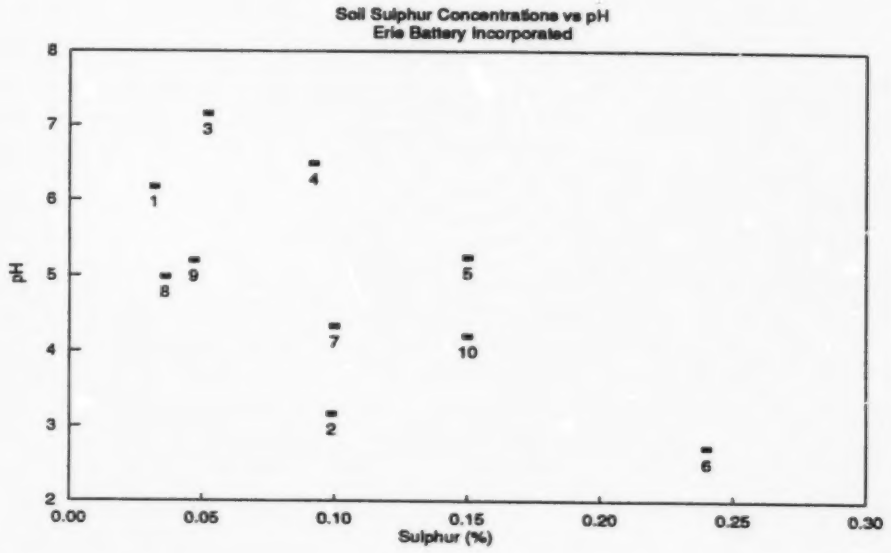

Figure 2j:

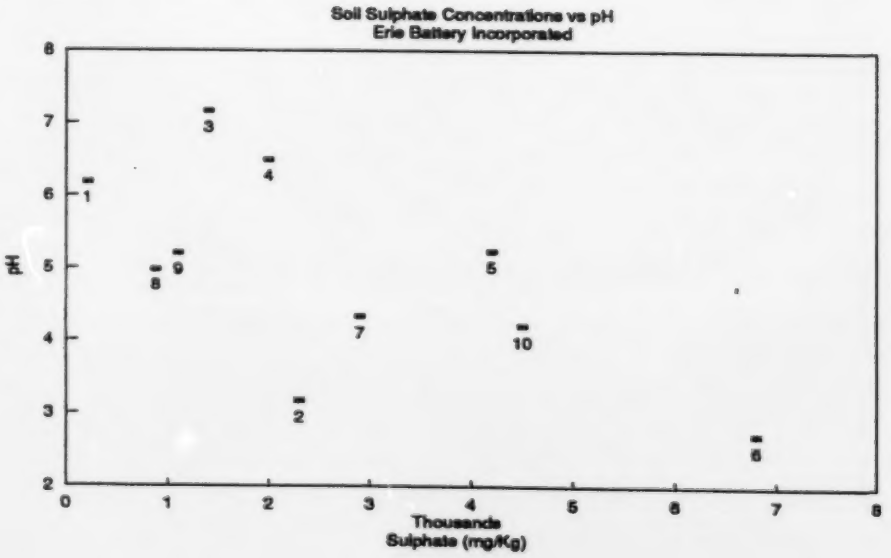

Table 3 clearly demonstrates the strong and consistent correlations between analytes associated with lead-acid battery solution. Sites with elevated lead concentrations also have high antimony, sulphur and sulphate; and low pH. Sites with lower concentrations of the analytes have higher pH.

A review of the ten scatter plots, Figures 2a through 2j, shows a tendency of Sites 1, 3, 4 and 8 to be clustered in the corner of the plots corresponding to the low contaminant concentrations or higher pH. Sites 1, 3 and 4, it should be recalled, were selected as sampling sites that were unlikely to have been influenced by the discharge of the solution from the loading dock. Site 8, on the other hand, was a site in the ditch, downhill from the alleged point of discharge.

At the other extreme, Site 6 consistently falls into the diametrically opposite corner of the plots, corresponding to high contaminant concentrations and acidified soil. Site 6 was selected as the site where discharge would have entered the ditch. The analytical data supports this scenario.

The remaining sites show intermediate degrees of contamination and acidification. Analytical data for these sites distinguish them as being distinct from those not influenced by the discharge. The irregular distributions shown by Sites 2, 5, 7, 9 and 10 suggest that variable amounts of residue were deposited by the discharge. This may be due to varying residence times (i.e. pooling) of the contaminating solution on the soil or differences in the affinity of the soil to adsorb the contaminants.

An examination of the data for the ditch Sites 6 through 10 found no clear contaminant gradient. The data indicate the deposition of lead-acid battery contaminants, but not in a consistent or sequential manner. Again, residence times and flow paths, which would be a function of micro-topography; and soil absorbtion affinities could account for the lack of a contaminant gradient. It should be noted that Site 8, which fell within the

group of unaffected sites in the scatter plots, is a ditch site. This sample was moderately acidic, but the contaminant concentrations were quite low.

During the collection of samples, an assessment was made of the extent of ditch that may have received the discharge flow and sampling sites were selected accordingly. Site 10 was the most distant downhill ditch site sampled. The analytical data shows that this site was influenced quite significantly. Consequently, it is not possible to delineate the extent of contamination along the ditch.

CONCLUSIONS

The soil in an area adjacent to the west side of a building occupied by Erie Battery Inc., and an undefined length of drainage ditch, have been contaminated by lead, antimony and sulphate; as well as being acidified. The contaminants are synonymous with those present in lead-acid storage battery solution. The degree, pattern and characteristics of the contamination supports the allegation that waste battery solution was discharged onto the ground.

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CERTIFICATE OF ANALYSIS

Issued To: W. Gizyn
Submission Number: TE4559
Laboratory Sample Number(s): CC20-0022 to CC20-0031
Date Sample(s) Received at Laboratory: May 13th, 1991

Analysis:

Laboratory Sample Numbers	Lead (mg/Kg)	Sulphur (%)	Sulphate (mg/Kg)	pH
CC20-0022	44	0.032	210	6.18
CC20-0023	260	0.099	2300	3.17
CC20-0024	45	0.052	1400	7.16
CC20-0025	82	0.092	2000	6.49
CC20-0026	440	0.15	4200	5.24
CC20-0027	840	0.24	6800	2.72
CC20-0028	760	0.10	2900	4.33
CC20-0029	100	0.036	880	4.98
CC20-0030	360	0.047	1100	5.20
CC20-0031	380	0.15	4500	4.20

Certified at Toronto, this 19th day of June, 1991.

L. Pastorek
Analyst

APPENDIX 2

Ontario

Ministry of the Environment | Ministère de l'Environnement

Laboratory Services Branch | Direction des services de laboratoire

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CERTIFICATE OF ANALYSIS

Issued To: W. Gizyn
Submission Number: TE4559
Laboratory Sample Number(s): CC20-0022 to CC20-0031
Date Sample(s) Received at Laboratory: May 13th, 1991

Results:

The following samples were analysed for antimony (Sb) by the standard technique.

Laboratory Sample Numbers	Antimony (Sb) mg/Kg
CC20-0022	0.4
CC20-0023	9.2
CC20-0024	0.4
CC20-0025	0.8
CC20-0026	3.4
CC20-0027	13
CC20-0028	4.2
CC20-0029	0.9
CC20-0030	2.0
CC20-0031	3.7

Certified at Toronto, this 24 day of September, 1991.

R. Sadana.
R. Sadana
Analyst

Derivation and Significance of the MOE Phytotoxicology "Upper Limits of Normal" Contaminant Guidelines.

The MOE Upper Limits of Normal (ULN) contaminant guidelines represent the expected maximum concentration in surface soil, foliage (trees and shrubs), grass, moss bags, and snow from areas in Ontario not exposed to the influence of a point source of pollution. Urban ULN guidelines are based on samples collected from developed urban centres, whereas rural ULN guidelines were developed from non-urbanized areas. Samples were collected by Phytotoxicology staff using standard sampling procedures (ref: Ontario Ministry of the Environment 1983, *Phytotoxicology Field Investigation Manual*). Chemical analyses were conducted by the MOE Laboratory Services Branch.

The ULN is the arithmetic mean, plus three standard deviations of the mean, of the suitable background data. This represents 99% of the sample population. This means that for every 100 samples which have not been exposed to a point source of pollution, 99 will fall within the ULN.

The ULNs do not represent maximum desirable or allowable limits. Rather, they are an indication that concentrations that exceed the ULN may be the result of contamination from a pollution source. Concentrations that exceed the ULNs are not necessarily toxic to plants, animals, or people. Concentrations that are below the ULNs are not known to be toxic.

ULNs are not available for all elements. This is because some elements have a very large range in the natural environment and the ULN, calculated as the mean plus three standard deviations, would be unrealistically high. Also, for some elements, insufficient background data is available to confidently calculate ULNs. The MOE Phytotoxicology ULNs are constantly being reviewed as the background environmental data base is expanded. This will result in more ULNs being established and may amend existing ULNs.